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NEW HIGH TEMPERATURE PLASMAS AND SAMPLE
INTRODUCTION SYSTEMS FOR ANALYTICAL
ATOMIC EMISSION AND MASS SPECTROMETRY

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Progress Report

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Table of Contents

Subject	Page
1. PURPOSE AND SCOPE	1
2. TECHNICAL PROGRESS FROM JANUARY-1993 THROUGH DECEMBER-1993	2
3. TECHNICAL PROGRESS EXPECTED NEXT YEAR	4
4. REFERENCES CITED	5
5. DOE-SPONSORED PUBLICATIONS AND PAPERS PRESENTED DURING 1992-93	6
6. TIME DEVOTED TO THE PROJECT AND DEVELOPMENT OF HUMAN RESOURCES	8
7. EDUCATIONAL SUPPORT	9

PROGRESS REPORT

In this Report, we summarize our DOE-sponsored research activities over the period January 1993 - December 1993. Only the most important achievements are included to illustrate our progress and obstacles. Detailed description of our investigations are outlined in the reprints and preprints that accompany this Report.

1. PURPOSE AND SCOPE

In this research, new high temperature plasmas and new sample introduction systems are explored for rapid elemental and isotopic analysis of gases, solutions, and solids using mass spectrometry (MS) and atomic emission spectrometry (AES). These studies offer promise of solving singularly difficult analytical problems that either exist now or are likely to arise in the future in the various fields of energy generation, environmental pollution, new material development, biomedicine and nutrition. During the period January 1993 - December 1993, emphasis was placed on:

- (a) **analytical investigations** of atmospheric-pressure helium inductively coupled plasmas (He ICPs) that are suitable for atomization, excitation, and ionization of elements possessing high excitation and ionization energies, for the purpose of enhancing the detecting powers of a number of elements;
- (b) **simulation and computer modeling** of plasma sources to predict their structure and fundamental and analytical properties, without incurring enormous cost for extensive experimental studies;
- (c) **spectroscopic imaging and diagnostic studies** of high-temperature plasmas, particularly new He ICP discharges, to instantly visualize their prevailing structure, to quantify key fundamental properties, and to verify predictions by mathematical models;
- (d) **fundamental studies** of He ICP discharges and argon-nitrogen plasmas by high-resolution Fourier transform spectrometry; and
- (e) **fundamental and analytical investigation** of new, low-cost devices as sample introduction systems for atomic spectrometry, and examination of new diagnostic techniques suitable for probing the aerosol over a wide range. Again, these endeavors are designed to ultimately improve analytical performance indices such as detection limits, precision, and the degrees of freedom from interferences.

2. TECHNICAL PROGRESS FROM JANUARY-1993 THROUGH DECEMBER-1993.

The funds provided by DOE (\$77.5 k) for this research were approximately one-half of the requested level when our renewal proposal was submitted last year. We emphasize here that the

funding level was controlled by the prevailing economic situation rather than comments by the reviewers. The proposed studies on the direct optical sampling of ultraviolet radiation from He ICP could not be pursued due to funding limitation. Relatedly, our promising fundamental studies of sample introduction systems, initiated during the previous grant period, had to be significantly curtailed [1,2]. We are hoping to acquire supplemental funds from DOE for these projects next year.

Despite the cited difficulty, we have made good progress in a number of the projects thanks to the efforts of PI's six graduate students. Our studies on ICP-MS were focused on He ICP discharges [3] using a crystal-controlled generator. This study demonstrated the first application of the He ICP as an ionization source for mass spectrometry for the determination of metals and nonmetals in aqueous solutions. The effect of four approaches for reducing the extent of secondary discharge in He ICP-MS were examined. These approaches included: i) the use of a center-tapped load coil, ii) modified load coils, iii) electrostatic shields, and iv) application of samplers made from nonconductive materials and aluminum. Analytical characteristics of the system such as the background mass spectrum for injection of nitric acid solution, effects of the length of the plasma confinement tube, forward power and injector gas flow rate on ion signal intensities, and the level of oxide and doubly-charged ions were determined. Isotope ratios for $^{63}\text{Cu}/^{65}\text{Cu}$, $^{58}\text{Ni}/^{60}\text{Ni}$ and $^{80}\text{Se}/^{78}\text{Se}$ were measured. The limits of detection, obtained with an analogue detector and a prototype spectrometer, for the metals studied were in the range 0.2-9 ng/mL while those for As, Br, Se, and I were 0.2, 1, 0.2 and 0.04 ng/mL, respectively, at 800 W forward power. Linear dynamic ranges of over four orders of magnitude were achieved. In a subsequent study [4], it was shown that the He ICP-MS system allows determination of certain isotopes that suffer from spectral interference in Ar ICP-MS.

Another avenue of research in He ICP-MS that we began to explore this year involved the use of a free-running generator (Sciex/Perkin-Elmer Corporation). With a free-running generator, impedance mismatch is minimized more rapidly than for crystal-controlled generators because the induction coil and the plasma form an integral part of the tank circuit. One notable feature of free-running generator is the ease with which a plasma is formed over the wide range of operating condition for the Ar ICP, especially under the *balanced circuit condition* required for He ICP-MS studies. Langmuir probe measurements indicate plasma potential of approximately + 1 V dc and 200 mV peak-peak of RF for the Ar ICP formed with the free-running generator marketed by Perkin-Elmer/Sciex Corporation [5]. This condition simplifies the extraction of ions from the helium plasma for delivery to ion optics inside the vacuum chamber of the ICP-MS. Thus far, we have formed an assortment of annular helium plasmas, with a wide range of apparent intensities, with the free-running generator. The new plasmas are not yet coupled to our mass spectrometer because a special heavy-duty X-Y-Z stage had to be first developed for positioning the RF generator with respect to the ICP-MS interface. We anticipate that the coupling process will be completed by the end of 1993. At any rate, the new helium plasmas formed with the

free-running generator are structurally different from the intense He ICPs that we have formed with crystal-controlled generators. Accordingly, these new helium plasmas present a new avenue of research for us and others because their analytical and fundamental properties are unexplored for many applications in the entire field of atomic and mass spectrometries. In our view, this development by itself is exciting because the research is speculative in nature, and thus the potential exists to realize some of the "anticipated" fundamental advantages of helium-based plasmas for aqueous sample introduction.

We now summarize some of our studies on He ICP-AES. Last year, we initiated a project for the construction of an imaging spectrometer. We have constructed a simple, inexpensive optical imaging spectrometer for the rapid acquisition of spatially-resolved information from He ICP discharges for comparison with the results from the Ar ICP [6]. The system uses a 35-cm focal length Czerny-Turner monochromator/spectrograph and a solid state charge-injection device (CID), having 388 by 488 sensor elements, to produce quantitative images of the plasmas. These lateral maps of emission intensity are then subjected to Abel inversion to produce radial emission intensity distribution maps. With a 15% image magnification, the entire image of the plasma can be monitored simultaneously with a spatial resolution of 0.16 and 0.09 mm in the horizontal and vertical directions, and a spectral resolution of 4 nm. Our imaging studies reveal that the most intense analyte emission in He ICP originate from the axial channel. With the increase in forward power, the maximum emission intensity zone shifts to a lower position along the axial channel. The location of this zone, however, seems to be a function of the upper state energy of the spectral line, moving to a higher observation heights for lines of high excitation energies. These studies are still in progress for the He ICP formed in our 13-mm torch. Work also has been extended this year to the investigation of two new He ICP discharges generated in an 18-mm torch and a 9-mm torch. The plasma in 18-mm torch is of interest for our He ICP-MS project because of the possibility to reduce air entrainment in the plasma. For the plasma in the 9-mm torch, the operating cost of He ICP can be reduced. At any rate, the availability of spatially-resolved data can significantly assist us in identifying zones within the plasma that are interesting and worthy of detailed probing. Also, such data can be used to check the accuracy of the predicted results obtained by mathematical modeling. In this respect, we have acquired this year new results for modeling helium plasmas in 9- and 18-mm torches. The results of some of these studies should be available for publication by the end of 1993. We intend to continue this line of work during the next grant period whenever plasmas in new He ICP torches are examined.

For the sake of brevity, we now list a number of other studies that have been completed or are still in progress:

- 1) Two accompanying preprints [7,8] present results of two sets of diagnostic studies on He ICP

and argon-nitrogen plasmas by high-resolution Fourier transform spectrometry.

- 2) An electronic paper [9] is being finalized for submission to *Spectrochimica Acta Electronica* by the end of this year. In this paper, we described a fast, revised algorithm for the calculation of electron number density (n_e) via least-squares fittings of spectral lines to the theoretical Stark-broadened profiles. The previous version of this copy-righted code has been used by many prominent investigators worldwide for diagnostic studies of plasmas. The substantially revised version of this program is prepared in C language for use on an IBM or compatible personal computers.
- 3) A paper on the computer modeling and simulation studies of He ICP discharges was published recently [10]. Another report [11] on the modeling and simulation of mixed-gas ICP discharges is being finalized for submission to *Spectrochimica Acta* by the end of this year. These studies were conducted in collaboration Professor J. Mostaghimi of University of Toronto.
- 4) As stated earlier, our proposed studies on sample introduction systems were curtailed due the lack of funding. Work was initiated on the study of a nozzle-type ultrasonic nebulizer in an attempt to reduce millisecond-type fluctuation in plasma spectrometry. Initial results of this study is to be presented at the 1993 FACSS Meeting [12]. In addition, two separate investigation were made on the utility of thimble-frit nebulizer and the humidifier-based ultrasonic nebulizer, developed during the previous grant period, for direct analysis of environmental samples and food. Results are being prepared for submission to the *Journal of Analytical Atomic Spectrometry* by the end of 1993 [13,14].

3. TECHNICAL PROGRESS EXPECTED NEXT YEAR

We anticipate that the on-going investigations discussed above will continue or expand next year. The results of some of these studies are being finalized for 6 publications (see papers number 16 to 21 in Section 5). A brief list of specific projects to be conducted next year is given below:

1. Currently, investigations of He ICP-MS is focussed on developing a more suitable He ICP-MS interface and using more robust helium plasmas. To achieve these goals, the following projects must be completed by next year: 1) increasing pumping capacity for the He ICP-MS interface by a factor of 3 to 5, 2) using new advanced ceramic materials or RF biasing of sampler to further reduce the pinch discharge at the sampler cone, 3) operating a more robust helium plasma that can be sustained at the interface for an extended period at power levels greater than 800 W, and 4) evaluating a He ICP formed in wide torch (such as 18-mm torch) to reduce air entrainment. The two most significant parameters to be measured in diagnostic studies of the He ICP-MS interface are plasma potentials and the mean kinetic energies of ions. The higher

- these quantities, the greater the interaction between the plasma and the mass spectrometer.
2. All of our measurements thus far have been based on positive ion detection. We have modified our mass spectrometer electronics for negative ion detection. The first phase of this study should be completed next year, with emphasis on halogens and nonmetals.
 3. We plan to explore the utility of He ICP discharges formed by a free-running generator as ion sources for mass spectrometry. This area is totally unexplored and there are possibilities for many applications in the entire field of atomic and mass spectrometries.
 4. Fundamental and analytical properties of He ICPs formed in 9- and 18-mm torches will be investigated. Results of these studies will be compared to data obtained through computer modeling and simulation of He ICPs using the LTE model. Because He ICP discharges are non-LTE plasmas, the proposed work will involve the analysis of kinetic non-equilibrium effects in He and He-H₂ analytical ICP discharges. As part of the work, thermophysical properties of helium and helium-hydrogen mixtures also will be calculated. We plan to calculate electron and atom/ion temperature, flow, electromagnetic fields, along with number densities of the electron, ion, neutral species for the He ICP.
 5. Assuming that supplemental funds become available, we propose to investigate new ultrasonic nebulizers (USNs) that don't lose efficiency at high viscosity, and USNs that generate nearly monodisperse aerosol from μ l quantity of sample solution. We also intend to conduct time-resolved measurements on aerosol prior to injection into plasmas to identify the nature of millisecond-type instabilities. Clearly, it is desirable to follow the fate of dry particles in plasmas as well.

4. REFERENCES CITED

1. R. H. Clifford, P. Sohal, H. Liu, and A. Montaser, *Spectrochim. Acta*, 47B, 1107 (1992).
2. R. H. Clifford, H. Tan, H. Liu, A. Montaser, F. Zarrin and P. B. Keady, "Particle Size Measurements in Submicron Range by Differential Electromobility Technique: Comparison of Aerosols from Thermospray, Ultrasonic, Pneumatic, and Frit-Type Nebulizers, *Spectrochim. Acta*, Part B, in press.
3. S. Nam, W. R.L. Masamba, and A. Montaser, "Investigation of Helium Inductively Coupled Plasma-Mass Spectrometry for the Detection of Metals and Nonmetals in Aqueous Solutions, *Anal. Chem.*, accepted for publication.
4. W. R.L. Masamba, S. Nam, and A. Montaser, "Helium Inductively Coupled Plasma-Mass Spectrometry: Matrix Effects Studies and the Determination of Arsenic and Selenium in Urine", in preparation for *Anal. Chem.*
5. S. Greenfield and A. Montaser, "Common RF Generators, Torches, and Sample Introduction

- Systems"; in *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*, A. Montaser, and D. W. Golightly, Eds, VCH, New York, Second Edition, 1992.
6. C. Hsieh, Anna-Lisa M. Boyes, and A. Montaser, "Monochromatic Imaging of Atmospheric-Pressure Helium Inductively Coupled Plasmas", *Spectrochim. Acta*, submitted.
 7. M. Cai, I. Ishii, R. H. Clifford, A. Montaser, B. A. Palmer and L. R. Layman, "Helium ICP Discharges: Spectral Line Widths and Temperatures Measured by High-Resolution Fourier Transform Spectrometry, *Spectrochim. Acta*, submitted.
 8. Ishii, M. Cai, A. Montaser, B. A. Palmer and L. R. Layman, " Rotational Temperatures of Argon-Nitrogen ICP Discharges Measured by High-Resolution Fourier Transform Spectrometry; *Spectrochim. Acta*, submitted.
 9. C. Hsieh, I. Ishii, H. Zhang, and A. Montaser. "A Revised, Fast, Flexible Algorithm for Determination of Electron Number Densities in Plasma Discharges ; in preparation for *Spectrochim. Acta Electronica*.
 10. M. Cai, A. Montaser, and J. Mostaghimi, *Spectrochim. Acta*, 48B, 789 (1993).
 11. M. Cai, A. Montaser, and J. Mostaghimi, "Modeling and Simulation of Argon-Nitrogen and Argon-Oxygen Inductively Coupled Plasmas", in preparation for *Spectrochim. Acta*, Part B.
 12. H. Liu, W. R. L. Masamba and A. Montaser, "Investigation of a Droplet Generator as a Sample Introduction System for Inductively Coupled Plasma Atomic Spectrometry", to be presented at the 1993 FACSS Meeting, Detroit, MD, October 1993.
 13. H. Liu, S. P. Dolan, and A. Montaser, "Application of a Disposable Thimble Frit Nebulizer for the Direct Analysis of Water Samples and Food", in preparation for *J. Anal. At. Spectrom.*
 14. H. Liu, S. P. Dolan, and A. Montaser, "Evaluation of a Low-Cost Humidifier-Based Ultrasonic Nebulizer for Direct Elemental Analysis of Environmental Samples by ICP-AES", in preparation for *J. Anal. At. Spectrom.*

5. DOE-SPONSORED PUBLICATIONS AND PAPERS PRESENTED DURING 1992-93

A) List of papers published, in press, submitted, or in preparation:

1. A. Montaser, Assessment of Potentials and Limitations of Plasmas Sources Compared to ICP Discharges in Analytical Spectrometry, in *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*, A. Montaser, and D. W. Golightly, Eds, VCH, New York, Second Edition, 1992.
2. A. Strasheim and A. Montaser, "Instrumentation for Optical Emission Spectrometry", in *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*, A. Montaser, and D. W. Golightly, Eds, VCH, New York, Second Edition, 1992.
3. S. Greenfield and A. Montaser, "Common RF Generators, Torches, and Sample Introduction

- Systems"; in *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*, A. Montaser, and D. W. Golightly, Eds, VCH, New York, Second Edition, 1992.
4. D. Demers and A. Montaser, "Analytical Application of the Inductively Coupled Plasma as an Atomization Cell for Atomic Fluorescence Spectrometry", in *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*, A. Montaser, and D. W. Golightly, Eds, VCH, New York, Second Edition, 1992.
5. A. Montaser, K. Ohls, and D. W. Golightly, "Inductively Coupled Plasmas in Gases Other Than Argon"; in *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*, A. Montaser, and D. W. Golightly, Eds, VCH, New York, Second Edition, 1992.
6. T. Hasegawa, M Umemoto, H. Haraguchi, C. Hsieh and A. Montaser, "Fundamental Properties of Inductively Coupled Plasmas"; ; in *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*, A. Montaser, and D. W. Golightly, Eds, VCH, New York, Second Edition, 1992.
7. A. Montaser and D. W. Golightly, Eds., *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*, VCH, New York, Second Edition, 1992, 1017 pages.
8. R. H. Clifford, P. Sohal, H. Liu, and A. Montaser, *Spectrochim. Acta*, 47B, 1107 (1992).
9. A. Montaser, Guest Editor for Mermet Honor Issue on "Research and Practical Spectrochemical Analysis", *Spectrochim. Acta*, 48B (1993).
10. M. Cai, A. Montaser, and J. Mostaghimi, *Spectrochim. Acta*, 48B, 789 (1993).
11. R. H. Clifford, H. Tan, H. Liu, A. Montaser, F. Zarrin and P. B. Keady, "Particle Size Measurements in Submicron Range by Differential Electromobility Technique: Comparison of Aerosols from Thermospray, Ultrasonic, Pneumatic, and Frit-Type Nebulizers, *Spectrochim. Acta*, Part B, in press.
12. S. Nam, W. R.L. Masamba, and A. Montaser, "Investigation of Helium Inductively Coupled Plasma-Mass Spectrometry for the Detection of Metals and Nonmetals in Aqueous Solutions, *Anal. Chem.*, accepted for publication.
13. M. Cai, I. Ishii, R. H. Clifford, A. Montaser, B. A. Palmer and L. R. Layman, "Helium ICP Discharges: Spectral Line Widths and Temperatures Measured by High-Resolution Fourier Transform Spectrometry, *Spectrochim. Acta*, submitted.
14. Ishii, M. Cai, A. Montaser, B. A. Palmer and L. R. Layman, " Rotational Temperatures of Argon-Nitrogen ICP Discharges Measured by High-Resolution Fourier Transform Spectrometry; *Spectrochim. Acta*, submitted.
15. C. Hsieh, Anna-Lisa M. Boyes, and A. Montaser, "Monochromatic Imaging of Atmospheric-Pressure Helium Inductively Coupled Plasmas", *Spectrochim. Acta*, submitted.
16. W. R.L. Masamba, S. Nam, and A. Montaser, "Helium Inductively Coupled Plasma-Mass Spectrometry: Matrix Effects Studies and the Determination of Arsenic and Selenium in Urine",

in preparation for Anal. Chem.

17. C. Hsieh, I. Ishii, H. Zhang, and A. Montaser, "A Revised, Fast, Flexible Algorithm for Determination of Electron Number Densities in Plasma Discharges ; in preparation for Spectrochim. Acta Electronica.
18. M. Cai, A. Montaser, and J. Mostaghimi, "Modeling and Simulation of Argon-Nitrogen and Argon-Oxygen Inductively Coupled Plasmas", in preparation for Spectrochim. Acta, Part B.
19. H. Liu, S. P. Dolan, and A. Montaser, "Application of a Disposable Thimble Frit Nebulizer for the Direct Analysis of Water Samples and Food", in preparation for J. Anal. At. Spectrom.
20. H. Liu, S. P. Dolan, and A. Montaser, "Evaluation of a Low-Cost Humidifier-Based Ultrasonic Nebulizer for Direct Elemental Analysis of Environmental Samples by ICP-AES", in preparation for J. Anal. At. Spectrom.
21. H. Zhang and A. Montaser, "RF-Powered Glow Discharge Atomic and Mass Spectrometry at 27 and 40 MHz" in preparation for Anal. Chem.

B) List of presentations at scientific meetings in 1993:

1. A. Montaser, "Plasmas Other Than Argon ICP Discharges for Analytical Spectrometry: Facts and Fictions", invited talk at the 1993 European Winter Conference on Plasma Spectrochemistry, Granada, Spain, January 1993.
2. S. Nam, W. R. L. Masamba, and A. Montaser "New Studies on Helium Inductively Coupled Plasma Mass Spectrometry", presented at the 1993 FACSS Meeting, Detroit, MD, October 1993.
3. M. Cai and A. Montaser, "Analytical and Fundamental Characteristics of a Helium ICP Formed in a 9-mm Torch", presented at the 1993 FACSS Meeting, Detroit, MD, October 1993.
4. H. Zhang and A. Montaser, "Determination of Halogens in Gaseous Samples by Helium Glow Discharge Spectrometry", presented at the 1993 FACSS Meeting, Detroit, MD, October 1993.
5. H. Liu, W. R. L. Masamba and A. Montaser, "Investigation of a Droplet Generator as a Sample Introduction System for Inductively Coupled Plasma Atomic Spectrometry", presented at the 1993 FACSS Meeting, Detroit, MD, October 1993.

6. TIME DEVOTED TO THE PROJECT AND DEVELOPMENT OF HUMAN RESOURCES.

PI devoted 100% of his time during two months of summer to this project. During the academic year, PI fulfilled his teaching duties but the remainder of his time was spent on the execution of this project and on the supervision of six graduate students.

7. EDUCATIONAL SUPPORT

This research will provide an excellent opportunity for the graduate students to broaden their knowledge base and contribute to the better understanding of analytical chemistry and physics of helium inductively coupled plasmas for spectrochemical analysis. Educational support is thus requested for two graduate students in the form of a stipend to enable them participate in the proposed research. This participation by the graduate students will be in connection with the preparation of any thesis or dissertation which is required by her/his academic program.

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